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**(54) Title:** HIGH INTERNAL PHASE EMULSIONS AND POROUS MATERIALS PREPARED THEREFROM**(57) Abstract**

A high internal phase emulsion having an emulsion stabilizing surfactant, one or more insoluble fillers, at least 70 volume percent of a discontinuous internal phase; and less than 30 volume percent of a continuous external phase containing one or more vinyl polymerizable monomer(s). Polymerizing the water-in-oil high internal phase emulsion produces an open-cell porous polymeric material having insoluble fillers incorporated into its polymeric backbone.

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HIGH INTERNAL PHASE EMULSIONS AND POROUS MATERIALS PREPARED THEREFROM

This invention relates to high internal phase emulsions and porous polymeric materials produced therefrom.

5 Emulsions are dispersions of discontinuous or discrete particles commonly referred to as the "internal" phase in a continuous or "external" phase. Emulsions can be either oil-in-water (o/w), having an oil internal phase and an aqueous external phase, or water-in-oil (w/o), having an aqueous internal phase and an oil external phase. Emulsions can contain as much as and more than 70 volume percent internal phase. These are often  
10 referred to as high internal phase emulsions (HIPEs). The volume fraction of the internal phase in such emulsions can be as high as 90 percent and frequently is as high as 95 percent with some HIPEs being reported as high as 98 percent aqueous phase.

An early application of high internal phase emulsions (HIPEs) is for a suspension medium for solids. See for example U.S. Patent 3,974,116. The high static  
15 viscosity of HIPEs prevents particles from settling. In a similar application, HIPEs have been used as transport fluids for particulates through pipelines. See for example U.S. Patent 3,617,095. Again, the high static viscosity of the emulsion prevents the solid particles from settling, yet the decreased viscosity while under shear allows the emulsion to be pumped efficiently through a pipeline. The ability to suspend particulates in HIPEs is somewhat  
20 surprising given the fact that particulates such as montmorillonite clays can be used to break emulsions, see for example K.J. Lissant, Emulsion and Emulsion Technology Part I; "Making and Breaking Emulsions"; pages 122-123 (1974).

The use of high internal phase emulsions (HIPEs) in forming porous polymeric materials is also well known and is described, for example, in U.S. Patents 5,210,104  
25 5,200,433; 4,536,521; 4,788,225; 5,147,345; 5,331,015; 5,260,345; 5,268,224 and 5,318,554. In the described HIPEs, the external oil phase typically comprises a vinyl polymerizable monomer, such as 2-ethylhexyl acrylate and styrene, and a cross-linking monomer such as divinylbenzene. The internal aqueous phase typically comprises water, a radical initiator (if not in the oil phase) and an electrolyte. To form a stable emulsion, a  
30 surfactant is added to the oil phase prior to emulsification. Commonly used emulsion stabilizing surfactants include, for example, nonionic surfactants, such as sorbitan esters (for example, sorbitan monooleate and sorbitan monolaurate). Other known stabilizing surfactants include certain polyglycerol aliphatic esters such as those described in U.S. Patent No. 5,500,451.

Porous polymeric materials prepared from HIPEs have been shown useful in many applications. For instance, U.S. Patents 5,260,345; 5,268,224; 5,331,015 teach the use of HIPE foams as absorbent materials for use in diaper-type articles. An attractive feature of HIPE foams for such an application is that their high void volume and low density provides a high capacity for liquid. For example, a 98 weight percent internal phase HIPE can produce a foam with approximately a 49 gram capacity for water per gram of foam (g/g capacity), assuming a polymer density of 1 g/cc. The g/g capacity of a foam can be increased either by increasing the void volume of the foam or by decreasing the density. Historically, one was changed by changing the other, that is, increasing the void volume decreased the density. Void volume is typically dictated by the internal phase ratio of the emulsion, the higher the internal phase ratio the higher the final void volume of the foam. One is limited, however, as to how high of an internal phase can be achieved and polymerized into a foam. Another method of increasing void volume in a HIPE foam is by including an inert oil in the external phase. After polymerization, the oil is removed, leaving voids in the polymer walls and struts. Collection and disposal of the inert oil, however, must be considered after the polymerization process. Furthermore, increasing the void volume tends to produce thinner struts in the foam walls thereby resulting in a weaker foam structure. Therefore, it would be advantageous to be able to increase the g/g capacity of a HIPE foam without increasing the internal phase ratio or using inert oils.

Another application for HIPE foams is as thermal and acoustical insulating materials. U.S. Patent 5,633,291, for instance, teaches the use of HIPE foams in these applications. For thermal insulating applications, it is important to hinder the transport of thermal energy through the insulating material. One path of thermal energy transport through material is radiative, in which the infrared wave is transmitted through the insulation directly to the other side. The thermal insulating ability of a HIPE foam would be enhanced if the radiative component could be diminished, or eliminated by the presence of an infrared blocking material. Thermal and acoustical insulating applications generally require flame retardant materials. However, HIPE foams are combustible because they are organic.

It would be desirable to provide a process whereby the g/g capacity of a HIPE foam can be increased without increasing the internal phase ratio or using inert oils. Further, it would be desirable to provide water-in-oil high internal phase emulsions and porous polymeric materials produced therefrom which incorporate infrared radiation blocking materials for enhancing the thermal insulating ability of the foam product. It would also be desirable to provide HIPE foams which incorporate flame retardant materials.

In a first aspect, this invention is a high internal phase emulsion having an emulsion stabilizing surfactant, an insoluble filler, at least 70 volume percent of an internal phase and less than 30 volume percent of an external phase containing one or more vinyl polymerizable monomers.

5           In a second aspect, the present invention is a process for preparing the high internal phase emulsion of the first aspect which comprises preparing an external phase, preparing an internal phase, adding an insoluble filler to one or both phases, and then mixing the internal phase with the external phase under conditions sufficient to form an emulsion.

10          In a third aspect, the present invention is a process for preparing the high internal phase emulsion of the first aspect which comprises preparing an external phase and an internal phase, mixing the aqueous phase with the oil phase under conditions sufficient to form an emulsion and then adding an insoluble filler to the emulsion.

In a fourth aspect, this invention is an open-cell porous polymeric material prepared by polymerizing the high internal phase emulsion of the first aspect.

15          In a fifth aspect, this invention is an open-cell porous polymeric material having insoluble fillers incorporated into its polymeric backbone.

We have discovered that high internal phase emulsions (HIPEs) can not only be prepared with insoluble fillers, but can also be polymerized into foams containing insoluble filler in the polymeric backbone. While HIPEs with selected insoluble fillers have been known, we have been able to prepare HIPEs with a broader spectrum of insoluble fillers including montmorillonite clays which are reported to break HIPEs (see reference above) and to incorporate them into a HIPE with vinyl polymerizable monomers. Furthermore, the fact that the HIPE can be polymerized into an open-celled foam and still retain the insoluble filler is surprising. In order to form open-celled structures, HIPEs must break to a certain extent during polymerization in order to create openings in the cell walls, but not break so much as to result in phase separation. Insoluble particulates, as noted above, have been known to break emulsions. Therefore, polymerizing a HIPE containing an insoluble particulate to an open-celled structure without resulting in phase separation is surprising.

30          The HIPEs of the present invention are useful in preparing polymeric foam materials with either increased or decreased densities without increasing or decreasing the internal phase ratio of the HIPE.

The polymeric foams of the present invention are also useful as thermal insulating materials and sound abatement materials as well as for fluid absorption.

Figure 1 is a comparison of sound attenuation spectra for the foams prepared in Example 6 and Comparative Example B.

- 5        The high internal phase emulsion (HIPE) of the present invention has greater than about 70 volume percent, more preferably, greater than about 90 volume percent and, most preferably, greater than about 95 volume percent of an internal phase; less than about 30 volume percent, more preferably, less than about 10 volume percent and, most preferably, less than about 5 volume percent of an external phase; and an insoluble filler.
- 10      Preferably, the HIPE is a water-in-oil emulsion comprising an aqueous internal phase and an oil external phase. HIPEs of as much as 98 volume percent or more of internal aqueous phase can be made by the present invention. The external phase comprises one or more vinyl polymerizable monomer. Preferably, the external phase also contains a cross-linking monomer. The internal phase comprises water. Typically, a water-soluble radical initiator is
- 15      added to the aqueous phase. If an oil-soluble initiator is employed, it is added to the oil phase. Additionally, the HIPE comprises a surfactant and an insoluble filler.

Vinyl polymerizable monomers which can be employed in the practice of the present invention are any polymerizable monomers having an ethylenic unsaturation. In general, the HIPEs are advantageously prepared from either or both (i) at least one monomer that tends to impart glass-like properties (glassy monomers) to the resulting porous polymeric material and (ii) at least one monomer that tends to impart rubber-like properties (rubbery monomers) to the resulting porous polymeric materials.

The glassy monomers are, for the purposes of the present invention, defined as monomeric materials which would produce homopolymers having a glass transition temperature above about 40°C. Preferred glassy monomers include methacrylate-based monomers, such as, for example, methyl methacrylate, and styrene-based monomers, such as, for example, various monovinyldene aromatics such as styrene, o-methylstyrene, chloromethylstyrene, vinyl ethylbenzene and vinyl toluene. More preferred glassy monomers include styrene, o-methylstyrene, and chloromethylstyrene. The most preferred glassy monomer is styrene.

The rubbery monomers are, for the purposes of the present invention, defined as monomeric materials which would produce homopolymers having a glass transition temperature of about 40°C or lower. Preferred rubbery monomers include alkyl esters of

ethylenically unsaturated acids ("acrylate esters" or "methacrylate" esters), such as 2-ethylhexyl acrylate, butyl acrylate, hexyl acrylate, butyl methacrylate, lauryl methacrylate, isodecyl methacrylate and mixtures thereof; vinyl aliphatic and alicyclic hydrocarbons such as butadiene; isoprene; and combinations of these comonomers. More preferred rubbery 5 monomers include butyl acrylate, 2-ethylhexyl acrylate, butadiene, isoprene and combinations of these comonomers. The most preferred rubbery monomer is 2-ethylhexyl acrylate.

Preferably, the HIPE emulsion includes at least one glassy monomer and at least one rubbery monomer. Without being bound by theory, it is believed that the rubbery 10 monomer provides the foams with flexibility and is used in an amount sufficient to allow compression, bending and twisting during processing, packaging, shipping, storing and use of articles containing such foams. It is believed the glassy monomer provides the foams with structural integrity and is used in an amount sufficient to minimize the incidence of foam tearing or fragmenting encountered when such foams are subjected to both dynamic and 15 static forces. The ratio of the glassy monomer to the rubbery monomer generally ranges from 1:25 to 1.5:1, more preferably from 1:9 to 1.5:1.

While the amount of the vinyl polymerizable monomers most advantageously employed depends on a variety of factors, such as the specific monomers, in general, the vinyl polymerizable monomer is used in an amount of from 50 to 100 weight percent, 20 preferably from 80 to 95 weight percent, and most preferably from 85 to 93 weight percent, based on the total external phase.

Insoluble fillers which can be employed in the practice of the present invention for preparing the HIPE include both inert and reactive fillers. The inert fillers are those which do not become copolymerized with the monomers used in preparation of HIPE foams. The 25 reactive fillers are those which become chemically attached to the molecular chains during polymerization. Inert fillers for use in this invention include for example, carbon black; graphite; metal hydroxides, such as aluminum hydroxide, magnesium hydroxide, calcium hydroxide, zirconium hydroxide, manganese hydroxide and iron hydroxide; metal powders such as iron powder; and hollow ceramic microspheres. An example of reactive fillers is 30 cross-linked polymeric materials with acrylate surface functionalities.

As used herein, the term "insoluble" means at least a finite amount of the material introduced into the system does not dissolve in either the external oil phase or the internal aqueous phase of the HIPE. Preferably at least 50 percent, more preferably at least

80 percent and most preferably 100 percent of the filler loading does not dissolve in either the external oil phase or the internal aqueous phase.

Hollow fillers, such as ceramic or glass microspheres can be used in the practice of the present invention. Hollow fillers can be prepared having a density below 1 g/cc. By incorporating such low density fillers into a HIPE foam, one may decrease the density (while simultaneously increasing the g/g capacity) without increasing the internal phase ratio of the HIPE precursor and without using inert oils in the external oil phase. Examples of hollow fillers include the various PQ Hollow Spheres available from The PQ Corporation (Valley Forge, PA) which range in density down to 0.13 g/cc.

Infrared blocking fillers such as carbon black and graphite powder can be used in the practice of the present invention and can reduce the infrared radiation transmitted through the final HIPE foam, increasing the effective thermal insulating value of the foam.

Organic and inorganic compounds containing phosphorus, antimony, boron, bismuth and halogens are known as fillers for increasing flame retardancy (see, for example, G.T. Gmitter, et al. Flexible Polyurethane Foams. In Plastic Foams: Part I; Frisch, K.C., Saunders, J.H., Eds.; Marcel Dekker, Inc.: New York, 1972; page 142) and can be used as fillers in the practice of the present invention. Other inorganic compounds useful as fire retardants in this invention include alumina trihydrate (also known as ATH, aluminum hydroxide,  $\text{Al(OH)}_3$ ) (see, for example, Hawley's Condensed Chemical Dictionary, 12<sup>th</sup> Edition, 1993, Richard J. Lewis, ed., p. 43), magnesium hydroxide and graphite. These inorganic compounds can be used alone or in conjunction with other organic or inorganic fire retardants.

Ferromagnetic materials, such as iron and nickel, can be incorporated to render magnetic properties to the final foam. A foam containing ferromagnetic materials can be useful, for example, in thermal and acoustical insulation on metal ceilings. A foam, for example, can be prepared with the ferromagnetic materials dispersed in a thin layer on one side of a foam. The ferromagnetic materials can either be magnetized before or after introduction into the foam. The foam composition can then be easily attached to a ceiling containing ferromagnetic materials without nails or glue. Alternatively, the ferromagnetic materials in the foam may remain unmagnetized and the foam then would be attracted to magnetized materials.

Water and/or oil swellable fillers, such as cross-linked sodium polyacrylate can also be used in the practice of the present invention as long as a HIPE can be made, preferably as long as the HIPE with the filler can be polymerized into a foam.

Metal oxide and metal carbonate can also be used as fillers in the practice of  
5 the present invention. Such materials include calcium oxide, magnesium oxide, zirconium oxide, titanium oxide, manganese oxide, iron oxide, aluminum oxide, calcium carbonate, magnesium carbonate, manganese carbonate, iron carbonate and zirconium carbonate.

Metal nitride, metal carbide and metal boride materials such as aluminum nitride, silicon nitride, iron nitride, silicon carbide, manganese carbide, iron carbide, iron  
10 boride, aluminum boride, manganese boride or other materials used in the preparation of ceramic materials may also be used in the practice of the present invention for preparing the HIPE. Mixtures of one or more such materials may also be employed.

Naturally occurring members of the clay mineral family or synthetic members of the clay mineral family can also be employed as fillers in the practice of the present  
15 invention. Such fillers include talc, mica and additional members of the clay mineral family such as montmorillonite, hectorite, kaolinite, dickite, nacrite, halloysite, saponite, nontronite, beidellite, volhonskoite, saucnite, magadiite, medmontite, kenyate, vermiculite, serpentines, chlorites, palygorskite, kulkeite, aliettite, sepiolite, allophane and imogolite can also be employed. Mixtures of one or more such materials may also be employed.

20 Other fillers which can be employed in the practice of the present invention include multilayered inorganic materials (conventionally referred to as "nanofillers"). The multilayered inorganic material which may be used in the practice of the invention can be any swellable layered inorganic material. Typically, the layered inorganic material is comprised of layers having two opposing faces which may be relatively flat or slightly curved.  
25 Such materials are described in U.S. Patent 4,889,885.

Representative examples of such swellable layered inorganic materials include members of the clay mineral family such as those described previously. Other representative examples of such swellable layered inorganic materials include illite minerals such as ledikite; the layered double hydroxides or mixed metal hydroxides such as  
30  $Mg_6Al_{3.4}(OH)_{18.8}(CO_3)_{1.7}H_2O$  (see W. T. Reichle, J. Catal., 94 (1985), 547), which have positively charged layers and exchangeable anions in the interlayer spaces; chlorides such as  $ReCl_3$  and  $FeOCl$ ; chalcogenides such as  $TiS_2$ ,  $MoS_2$ , and  $MoS_3$ ; cyanides such as  $Ni(CN)_2$ ; and oxides such as  $H_2Si_2O_5$ ,  $V_5O_{13}$ ,  $HTiNbO_5$ ,  $Cr_{0.5}V_{0.5}S_2$ ,  $W_{0.2}V_{2.8}O_7$ ,

$\text{Cr}_3\text{O}_8$ ,  $\text{MoO}_3(\text{OH})_2$ ,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaPO}_4\text{CH}_3 \cdot \text{H}_2\text{O}$ ,  $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ .

Mixtures of one or more such materials may also be employed.

Depending on the application of the final foam, the preferred insoluble fillers are carbon black, graphite, metal powders, metal hydroxides, hollow fillers such as glass or 5 ceramic microspheres, natural or synthetic clays, nanofillers, powders of metals, flame retardant fillers such as those containing phosphorus, antimony, boron, bismuth and/or halogens, copolymerizable fillers such as acrylate functionalized polymeric powders, oil swellable fillers such as lightly cross-linked polymeric powders, and aqueous swellable materials such as cross-linked sodium polyacrylate. The more preferred insoluble fillers are 10 carbon black, graphite powder, metal powders, metal hydroxides, hollow ceramic microspheres, nanofillers, and powders of metals. The most preferred insoluble fillers are carbon black, graphite, aluminum trihydroxide, magnesium hydroxide, hollow ceramic microspheres, Clayton APA Montmorillonite silicate clay, and iron powder.

Insoluble fillers can modify many characteristics of a HIPE foam including 15 density, modulus, tensile strength, thermal conductivity, flame retardancy, and magnetic property. Typically, more than one property is modified upon incorporation of a single insoluble filler. For example, incorporation of a large volume of iron powder will simultaneously increase the density of a foam and increase its ferromagnetic property. Often, large amounts of insoluble filler will tend to decrease the tensile strength of the foam. 20 This tensile strength loss is suspected to arise from weak adhesion between the polymer and the filler. A reduction in tensile strength can be countered by using a filler which chemically or mechanically binds into the polymeric network. One example is to modify the surfaces of the filler with a coupling agent, many of which are well known in the art. Known coupling agents include organofunctional silicon compounds such as vinyl trimethoxy silane 25 and  $\gamma$ -methacryloxypropyl trimethoxy silane, and titanium compounds such as and isopropyl triisostearoyl titanate and isopropyl trimethacryl titanate. The methacrylate functional coupling agent could be especially effective as the methacryl groups take part in the polymerization reaction. Another example is to use an acrylate functionalized filler which will copolymerize with the monomers during polymerization. Fillers which are swellable in the 30 organic monomer can become strongly bound mechanically as monomer polymerized through the swollen filler particle.

The amount of insoluble filler most advantageously employed depends on a number of factors including the desired application of the HIPE or polymerized HIPE foam and the type of filler used. As previously described, often more than one property of a foam

is modified when a filler is incorporated. Thus, the amount of filler employed must be adjusted to achieve the desired property. For example, if one desires a dense foam with ferromagnetic properties they could prepare a HIPE with large amounts of iron powder. However, if a person wants ferromagnetic properties but does not desire high density they  
5 could use much less iron powder, or prepare a layered structure with iron powder in a thin layer and hollow, low density filler in another layer. Some fillers require a higher concentration than others to reach a desired effect. For example, carbon black can significantly effect the thermal conductivity of a foam at a loading of less than 15 weight percent while approximately 30 weight percent or more ATH must be used to notice a  
10 significant increase in flame retardancy. Therefore, the application and type of filler used plays a role in determining optimal filler concentrations. In general, the insoluble filler can be employed in an amount up to and exceeding 100 volume percent relative to the continuous phase. A broader domain of insoluble fillers can be employed up to 100 volume percent relative to the continuous phase; an even broader domain of insoluble fillers can be  
15 employed up to 50 volume percent relative to the continuous phase; a still broader domain of insoluble fillers can be employed up to 10 volume percent relative to the continuous phase; and the broadest domain of insoluble fillers can be employed up to 1 volume percent relative to the continuous phase.

Cross-linking monomers which can be employed in the practice of the present  
20 invention for preparing the HIPE include any multifunctional unsaturated monomers capable of reacting with the vinyl monomers. Multifunctional unsaturated cross-linking monomers include, for example, divinylbenzene, ethylene glycol dimethacrylate, 3-butylene dimethacrylate, trimethylolpropane triacrylate and allyl methacrylate. While the amount of cross-linking monomers most advantageously employed depends on a variety of factors,  
25 such as the desired polymer modulus, in general, the cross-linking monomer is used in an amount of from 0 to 50 weight percent, preferably from 5 to 20 weight percent, and most preferably from 7 to 15 weight percent, based on the total external phase.

Radical initiators which can be employed in the practice of the present  
invention for preparing the HIPE include the water-soluble initiators such as, for example,  
30 potassium or sodium persulfate and various redox systems such as ammonium persulfate together with sodium metabisulfite and oil-soluble initiators, such as, for example, azobisisobutyronitrile (AIBN), benzoyl peroxide, methyl ethyl ketone peroxide and di-2-ethylhexyl-peroxydicarbonate and lauroyl peroxide. The initiator can be added to the aqueous phase or to the oil phase, depending on whether the initiator is water-soluble or oil-soluble.

The initiator should be present in an effective amount to polymerize the monomers.

Typically, the initiator can be present in an amount of from 0.005 to 20 weight percent, preferably from 0.1 to 10 weight percent and most preferably from 0.1 to 5 weight percent, based on total monomers.

5           The aqueous phase can include a water-soluble electrolyte for aiding the surfactant in forming a stable emulsion, controlling porosity of the foam and/or enhancing the hydrophilicity of the resulting polymeric foam material if left as a residual component of the foam material. Water-soluble electrolytes which can be employed in the practice of the present invention include inorganic salts (monovalent, divalent, trivalent or mixtures thereof),  
10          for example, alkali metal salts, alkaline earth metal salts and heavy metal salts such as halides, sulfates, carbonates, phosphates and mixtures thereof. Such electrolytes include, for example, sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, lithium chloride, magnesium chloride, calcium chloride, magnesium sulfate, aluminum chloride and mixtures thereof. Mono- or divalent salts with monovalent anions, such as halides, are  
15          preferred. While the amount of electrolytes most advantageously employed depends on a variety of factors, such as the specific compound, the desired porosity of the foam and the surfactant employed, in general, the electrolytes can be employed up to 20, more preferably up to 5 and most preferably up to about 1 weight percent, based on the total aqueous mixture.

20          The aqueous phase can additionally comprise a non-electrolyte component, such as, for example, glycerin, as long as a HIPE can still be prepared and polymerized into a foam.

Surfactants which can be employed in the practice of the present invention for preparing water-in-oil high internal phase emulsions include nonionic surfactants, such as,  
25          for example, sorbitan esters, including sorbitan monooleate and sorbitan monolaurate; glycerol esters, such as glycerol monooleate; PEG 200 dioleate, partial fatty acid esters of polyglycerol; cationic surfactants, such as ammonium salts; and anionic surfactants, such as certain organic sulfate and sulfonate compounds. Also suitable are polymerizable surfactants such as those described in copending Application Serial No. 558,333, filed  
30          November 15, 1995. Such surfactants include surfactants having polymerizable vinyl groups and surfactants capable of undergoing a graft reaction (graftable surfactants) at the conditions of polymerization. Also suitable are the poly(butylene oxide/ethylene oxide) sulfate-based surfactants described in copending Provisional Application Serial No. 60,046,910 filed May 16, 1997.

The amount of surfactant used must be such that a high internal phase emulsion will form. Generally, the amount of surfactant needed varies with the specific surfactant and the type of formulation used. As little as about 0.125 weight percent, or less, based on continuous phase can be used. More generally, as little as about 0.25 weight  
5 percent based on continuous phase can be used. Generally, up to about 25 weight percent or more, based on the continuous phase, can be used, if desired.

Methods for preparing water-in-oil emulsions are known in the art such as, for example, in U.S. Patents 4,522,953 and 5,210,104, and these methods can be employed in the practice of the present invention. For example, the water-in-oil HIPE can be prepared in  
10 batches. In general, to form a water-in-oil HIPE in batch quantities, the water phase is gradually added to a mixture of oil phase and surfactant while the mixture is being agitated. Agitation can be accomplished any number of ways including impeller-type agitation. Alternatively, water-in-oil HIPEs can be prepared in a continuous flow manner. Methods for continuous flow HIPE preparation are also well established in the literature. See, for  
15 example, U.S. Patents 4,018,426 and 5,198,472.

Incorporation of insoluble fillers into the HIPE can be done prior to or after emulsification. If incorporated prior to emulsification, the insoluble filler can typically be added to the oil phase or aqueous phase or to both phases. The insoluble filler can be added as a separate phase during the emulsification process, particularly in a continuous  
20 flow procedure. Alternatively, the filler can be mixed into the emulsion after the emulsion has been formed. The preferred method of incorporating the filler depends on a number of factors including the emulsification procedure used and the type and amount of filler used. For example, an insoluble filler which does not disperse into an aqueous phase would not be optimally incorporated into the emulsion by adding it to the aqueous phase prior to  
25 emulsification. Such a filler would be better incorporated into the emulsion by either adding it to the oil phase, adding it as a separate phase, or adding it after polymerization.

Layered foam compositions can be prepared from the HIPE of the present invention in accordance with the process described in copending Provisional Application Serial No. 60/055,852 filed August 15, 1997. For example, a layered foam composition can  
30 be prepared comprising two or more layers with differing amounts or types of fillers. One application where layered filled foams are useful is in sound abatement. Layered compositions with iron sponge powder in one layer and hollow ceramic microspheres in another have demonstrated enhanced sound attenuation properties over similar foams

prepared without fillers, with only the iron or only the microspheres, or with a homogeneous mix of iron powder and ceramic microspheres.

The following working examples are given to illustrate the invention and should not be construed to limit its scope. Unless otherwise indicated, all parts and

5 percentages are by weight.

#### Example 1 - HIPE Foam with Montmorillonite Silicate Clay

Clayton APA Montmorillonites Silicate Clay (a montmorillonite silicate clay available from Southern Clay Products, Inc.) was mixed to a 2-weight percent concentration into a monomer mix comprising 64 weight percent 2-ethylhexyl acrylate, 14 weight percent

10 styrene, and 22 weight percent divinylbenzene (55 percent active). Into 4.6 grams of the monomer/clay mix was dissolved 1.1 grams SPAN™ 80 (sorbitan monooleate) and 0.35 g SPAN™ 85 (sorbitan trioleate). A separate aqueous phase was prepared comprising 114 g water, 1.1 g calcium chloride dihydrate and 0.3 g potassium persulfate. The aqueous phase was added dropwise to the monomer/clay/surfactant mix while stirring at 300 RPM using a  
15 three-paddle mixer. A thick white HIPE was produced. The HIPE was polymerized at 60°C for 16 hours in a PYREX® dish covered with Saran Wrap™ (Trademark of The Dow Chemical Company). The sample was soaked in 2-propanol until it can be compressed free of the internal aqueous phase. Three rinses were done in the 2-propanol, three rinses in water, and a final rinse again in 2-propanol. The sample was squeezed between paper  
20 towels and allowed to dry at room temperature. The final foam was expanded, compressible and resilient.

#### Example 2 - HIPE Foam with Iron Powder

An oil phase was prepared by mixing 6.75 g 2-ethylhexyl acrylate, 4.62 g styrene, 1.13 g divinylbenzene (55 percent active), 2.50 g SPAN 80 (sorbitan monooleate),  
25 and 0.10 g lauroyl peroxide. An aqueous phase was prepared by mixing 133.65 g water,

1.35 g calcium chloride dihydrate, and 0.70 g potassium persulfate. A HIPE was prepared by adding the aqueous phase dropwise to the oil phase while mixing at 300 RPM with a three-paddle mixer. The HIPE was mixed an additional 2 minutes after forming to ensure homogeneity. To the HIPE was added 20 g of ANCOR B iron sponge powder (Hoeganaes,  
30 Inc.; Valley Forge, PA) while continuing the mixing. The resulting gray emulsion was polymerized at 65°C for 20.5 hours in a PYREX dish covered with Saran Wrap™. The resulting foam was squeezed free of aqueous phase and rinsed three times in 2-propanol,

three times in water, and a final time in 2-propanol. The cleaned foam was squeezed free of alcohol and allowed to air-dry. The resulting foam has iron powder incorporated in its polymer matrix and was attracted to a magnet.

Example 3 - HIPE foam with Hollow Ceramic Microspheres

5 An oil phase was prepared by mixing 17.9 g 2-ethylhexyl acrylate, 12.25 g styrene, 3.00 g divinylbenzene (55 percent active), 6.63 g SPAN 80 (sorbitan monooleate), and 0.27 g lauroyl peroxide. An aqueous phase was prepared by mixing 354.51 g water, 3.58 g calcium chloride dihydrate, and 1.86 g potassium persulfate. A HIPE was prepared by adding the aqueous phase dropwise to the oil phase while mixing at 300 RPM with a  
10 three-paddle mixer. The HIPE was mixed an additional 2 minutes after forming to ensure homogeneity. Into the HIPE was mixed 8.95 g of hollow ceramic microspheres (SL-150 Extendospheres®, The PQ Corporation) using the three-paddle mixer at 300 RPM. The HIPE was polymerized at 65°C for 18 hours in a PYREX dish covered with Saran Wrap™. The resulting foam was squeezed free of aqueous phase and rinsed three times in 2-  
15 propnaol, three times in water, and a final time in 2-propanol. The cleaned foam was squeezed free of alcohol and allowed to air-dry.

Example 4 - Foam with Iron Powder and Hollow Ceramic Microspheres

An oil phase was prepared by mixing 17.90 g 2-ethylhexyl acrylate, 12.25 g styrene, 3.00 g divinylbenzene (55 percent active), 0.27 g lauroyl peroxide and 6.63 g SPAN  
20 80 (sorbitan monooleate). An Aqueous phase was prepared by mixing 354.51 g water, 3.58 g calcium chloride dihydrate, and 1.86 g potassium persulfate. The aqueous phase was added dropwise while mixing the oil phase at 300 RPM with a three-paddle mixer. Once the aqueous phase was completely added and while continuing mixing, 4.48 g ceramic  
25 microspheres and 14.38 g iron sponge powder was mixed into the emulsion. The resulting HIPE was mixed an additional 2 minutes to insure homogeneity. The emulsion was put into a PYREX dish, covered with Saran™ Wrap and polymerized in a forced-air oven at 65°C overnight. The resulting foam was squeezed free of aqueous phase and rinsed three times in 2-propanol, three times in water, and again in 2-propanol. The rinsed foam was squeezed free of most of the 2-popanol and allowed to air-dry to an expanded foam.

30 Example 5 - And Comparative Example A

Two HIPE foams were prepared and tested for their flame retardancy.

Comparative Example A - Control with no Filler

An oil phase was prepared by mixing 8.67 g 2-ethylhexyl acrylate, 1.90 g styrene, 2.98 g divinylbenzene (55 percent active), 1.45 g SPAN™ 80 (sorbitan monooleate), and 0.06 g lauroyl peroxide. A water phase was prepared by mixing

- 5      132.96 g water, 1.34 g calcium chloride dihydrate, and 0.64 g potassium persulfate. The aqueous phase was added dropwise to the oil phase while mixing at 300 RPM using a three-paddle mixer. The emulsion was mixed an additional 5 minutes after all of the aqueous phase was added to ensure homogeneity. The emulsion was put into PYREX dishes, covered Saran™ wrap, and polymerized in a forced-air oven at 65°C for 16 hours. The  
10     resulting foam was rinsed 3 times in 2-propanol (IPA), 3 times in water, and again in IPA. The final foam was squeezed free of most of the IPA and then dried in a vacuum oven at 80°C for several hours. The expanded foam was then allowed to set at room temperature for 2 days.

Example 6 - HIPE with Aluminum Trihydroxide (Al(OH)<sub>3</sub>) Filler

- 15     An oil phase was prepared by mixing 4.65 g 2-ethylhexyl acrylate, 1.02 g styrene, 1.60 g divinylbenzene (55 percent active), 1.45 g SPAN 80 (sorbitan monooleate), and 0.06 g lauroyl peroxide. Into this oil phase was mixed 6.30 g aluminum trihydroxide. An aqueous phase was prepared by mixing 132.96 g water, 1.34 g calcium chloride dihydrate, and 0.64 g potassium persulfate. The aqueous phase was added dropwise to the oil phase  
20     while mixing with a three-paddle mixer at 300 RPM in a polypropylene beaker. Once all of the aqueous phase was added, the emulsion was mixed an additional 5 minutes to insure homogeneity. The emulsion was poured into PYREX dishes, covered with Saran Wrap™ and placed in a forced-air oven at 65°C for 16 hours. The resulting foam was compressed free of most of the aqueous phase. The foam was rinsed and dried as described in  
25     Comparative Example A, producing an expanded foam.

Flame Retardancy Testing

- Foam samples of Comparative Example A and Example 5 were cut into strips 8 cm long, 1.5 cm wide, and approximately 5 mm thick. The sample strips were mounted vertically, clamped at the bottom and extending 7 cm upwards. The top of the foam was lit  
30     with a match. Observations were recorded below and demonstrate the flame retardant effect of the Al(OH)<sub>3</sub>.

Comparative Example B - Foam - Blank

The foam was easily ignited and burned down the entire 7 cm in 17 seconds, with near complete incineration in about 35 seconds.

Example 7 - Foam - ATH Filled Foam

- 5           The foam was difficult to ignite. Once ignited, the flame self-extinguished in 1 minute and 16 seconds having only burned the top 2 cm of the foam strip.

Example 8 - and Comparative Example C

Two HIPE foams were prepared and evaluated for their sound attenuation properties.

10          Comparative Example C – Non-filled Foam

An oil phase was prepared by mixing 17.90 g 2-ethylhexyl acrylate, 12.25 g styrene, 3.00 g divinylbenzene (55 percent active), 0.27 g lauroyl peroxide and 6.63 g SPAN 80 (sorbitan monooleate). An Aqueous phase was prepared by mixing 354.51 g water, 3.58 g calcium chloride dihydrate, and 1.86 g potassium persulfate. The aqueous phase was added dropwise while mixing the oil phase at 300 RPM with a three-paddle mixer. The resulting HIPE was mixed an additional 2 minutes to insure homogeneity. The emulsion was put into a PYREX dish, covered with Saran™ Wrap and polymerized in a forced-air oven at 65°C overnight. The resulting foam was squeezed free of aqueous phase and rinsed three times in 2-propanol, three times in water, and again in 2-propanol. The rinsed foam was squeezed free of most of the 2-propanol and allowed to air-dry to an expanded foam.

Example 9 – Layered Filled Foam

Two HIPEs were prepared, layered, and then polymerized. The bottom layer was prepared similar to that in Comparative Example C except 28.76 g ANCOR grade B iron sponge powder was mixed into the emulsion once it was formed. This bottom layer HIPE was placed into a PYREX dish. On top of the bottom layer was placed a thin sheet of polypropylene non-woven material. A second HIPE was prepared as described in Example 3. The second HIPE was carefully deposited over the polypropylene non-woven covering the bottom layer and the composition was polymerized in a forced-air oven at 65°C overnight. The final foam structure was carefully squeezed free of aqueous internal phase and rinsed three times with 2-propanol, three times with water, and again with 2-propanol.

The rinsed foam was squeezed free of 2-propanol and allowed to dry to an expanded layered structure.

The sound attenuation was determined for the foams prepared in Comparative Example B and Example 6 using a laboratory sound attenuation apparatus.

- 5 The apparatus basically comprises a source chamber, a receiver chamber, and a test sample fixture between the source and receiver chamber. A 3-inch diameter aperture was provided in the fixture. The source chamber was equipped with speakers and a microphone.
- 10 collected at the microphone in the receiver chamber with and without a sample blocking the aperture. The sound attenuation was defined as:

$$10 \log (I_0/I)$$

- where  $I_0$  was the sound intensity spectrum recorded without a sample in place and  $I$  was the sound intensity spectrum recorded with a sample in place. The sound attenuation spectra for the foam samples were presented in Figure 1 and reveals an improved sound attenuation for the layered foam structure over the comparative foam.
- 15

CLAIMS:

1. A high internal phase emulsion having an emulsion stabilizing surfactant, one or more insoluble fillers, at least 70 volume percent of a discontinuous internal phase, and less than 30 volume percent of a continuous external phase containing 5 one or more vinyl polymerizable monomers.

2. The high internal phase emulsion of Claim 1 wherein the emulsion is a water-in-oil emulsion.

3. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers has a density of less than 1 g/cc.

10 4. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers has a density of greater than 1 g/cc.

5. The high internal phase emulsion of Claim 2 wherein the surfactant is a sorbitan ester, glycerol ester, partial fatty acid ester of polyglycerol; a surfactant having polymerizable vinyl groups; a surfactant capable of undergoing a graft reaction at the 15 conditions of polymerization; or a poly(butylene oxide/ethylene oxide) sulfate-based surfactant.

6. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers is a flame retardant filler, an infra-red absorbing filler, and/or a ferromagnetic material.

20 7. The high internal phase emulsion of Claim 6 wherein the flame retardant filler is aluminum trihydrate, or a compound containing phosphorus, antimony, boron, bismuth or halogen; the infrared absorbing filler is carbon black and the ferromagnetic material is iron or nickel.

25 8. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers is a metal oxide, metal hydroxide, metal carbonate, metal nitride, metal carbide, metal boride, metal powder, hollow ceramic microsphere or hollow glass microsphere.

9. The high internal phase emulsion of Claim 8 wherein the metal oxide is calcium oxide, magnesium oxide, zirconium oxide, titanium oxide, manganese oxide, iron oxide or aluminum oxide; the metal hydroxide is aluminum hydroxide, magnesium hydroxide, calcium hydroxide, zirconium hydroxide, manganese hydroxide or iron hydroxide; the metal carbonate is calcium carbonate, magnesium carbonate, manganese carbonate, iron carbonate or zirconium carbonate; the metal nitride is aluminum nitride, silicon nitride or iron nitride; the metal carbide is silicon carbide, manganese carbide, iron carbide; the metal boride is iron boride, aluminum boride, manganese boride and the metal powder is iron powder.

10 10. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers is a naturally occurring or a synthetic member of the clay mineral family.

11. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers is talc, mica, montmorillonite, hectorite, kaolinite, dickite, nacrite, halloysite, saponite, nontronite, beidellite, volhonskoite, saucomite, magadiite, medmontite, kenyaita, vermiculite, serpentines, chlorites, palygorskite, kulkeite, aliettite, sepiolite, allophane, imogolite or mixtures thereof.

12. The high internal phase emulsion of Claim 1 wherein at least one of the insoluble fillers is a multilayered inorganic material.

13. The high internal phase emulsion of Claim 12 wherein the multilayered inorganic material is a member of the clay mineral family, an illite mineral, a layered double hydroxide, a mixed metal hydroxide, a chloride, or an oxide.

14. The high internal phase emulsion of Claim 13 wherein the illite mineral is ledikite; the mixed metal hydroxide is  $Mg_6Al_{3.4}(OH)_{18.8}(CO_3)_{1.7}H_2O$ ; the chloride is  $ReCl_3$  or  $FeOCl$ ; and the oxide is  $H_2Si_2O_5$ ,  $V_5O_{13}$ ,  $HTiNbO_5$ ,  $Cr_{0.5}V_{0.5}S_2$ ,  $W_{0.2}V_{2.8}O_7$ ,  $Cr_3O_8$ ,  $MoO_3(OH)_2$ ,  $VOPO_4 \cdot 2H_2O$ ,  $CaPO_4CH_3 \cdot H_2O$ ,  $MnHAsO_4 \cdot H_2O$ ,  $Ag_6Mo_{10}O_{33}$  or mixtures thereof.

15. The high internal phase emulsion of Claim 1 wherein the insoluble filler is present in an amount greater than 100 volume percent, based on the continuous phase.

16. The high internal phase emulsion of Claim 1 wherein the insoluble filler is present in an amount of from 1 to 100 volume percent, based on the continuous phase.

17. The high internal phase emulsion of Claim 1 wherein the insoluble filler is present in an amount of from 1 to 10 volume percent, based on the continuous phase.

18. A multilayer high internal phase emulsion comprising distinct layers wherein one or more layer contains one or more insoluble filler.

5 19. The emulsion of Claim 18 wherein the filler in each layer is present in an amount which is the same as or different from the amount of filler in each of the other layers.

10 20. A process which comprises preparing a continuous phase containing at least one vinyl polymerizable monomer, preparing an internal phase, introducing an insoluble filler into either the continuous phase or internal phase, or both, and then mixing the internal phase with the continuous phase under conditions sufficient to form an emulsion.

21. The process of Claim 20 wherein the emulsion is a water-in-oil emulsion comprising an oil continuous phase and an aqueous internal phase.

15 22. A process which comprises preparing a continuous phase containing at least one vinyl polymerizable monomer, preparing an internal phase and then mixing the internal phase with the continuous phase while simultaneously adding one or more insoluble fillers under conditions sufficient to form an emulsion.

23. The process of Claim 22 wherein the emulsion is a water-in-oil emulsion comprising an oil continuous phase and an aqueous internal phase.

20 24. A process which comprises preparing a continuous phase containing at least one vinyl polymerizable monomer, preparing an internal phase and then mixing the internal phase with the continuous phase under conditions sufficient to form an emulsion and then adding to the emulsion one or more insoluble fillers.

25. The process of Claim 24 wherein the emulsion is a water-in-oil emulsion comprising an oil continuous phase and an aqueous internal phase.

26. A process comprising preparing at least two high internal phase emulsions, at least one of which contains one or more insoluble filler, and then depositing each emulsion on top of each other thereby producing a layered high internal phase emulsion.

27. A porous polymeric material prepared by polymerizing the high internal phase emulsion of Claim 1.

28. A porous polymeric material prepared by polymerizing the high internal phase emulsion of Claim 2.

5 29. A porous polymeric material prepared by polymerizing the multilayer high internal phase emulsion of Claim 18.

30. An open-cell porous polymeric material having insoluble fillers incorporated into its polymeric backbone.

31. An article comprising the porous polymeric material of Claim 28.

10 32. An article comprising the porous polymeric material of Claim 29.

33. A multilayer polymeric foam comprising at least two layers, each layer being either physically or structurally different from that of a contiguous layer and at least one layer being formed from a high internal phase emulsion having one or more insoluble fillers, at least 70 volume percent of an internal phase and less than 30 volume percent of an 15 external phase containing one or more vinyl polymerizable monomers.

34. An article comprising a multilayer polymeric foam having at least two layers, each layer being either physically or structurally different from that of a contiguous layer and at least one layer being formed from a high internal phase emulsion having one or more insoluble filler, at least 70 volume percent of an internal phase and less than 30 volume 20 percent of an external phase containing one or more vinyl polymerizable monomers.

35. The article of Claim 34 in the form of an acoustical insulating material.

36. The high internal phase emulsion of Claim 1 wherein one or more insoluble filler is water-swellable or oil-swellable.

37. The high internal phase emulsion of Claim 1 wherein at least one of the 25 insoluble fillers has vinyl polymerizable functionalities capable of copolymerizing with the monomers in the emulsion.

38. The high internal phase emulsion of Claim 1 wherein the insoluble filler is present in an amount from less than 3 to 50 volume percent based on the external phase.

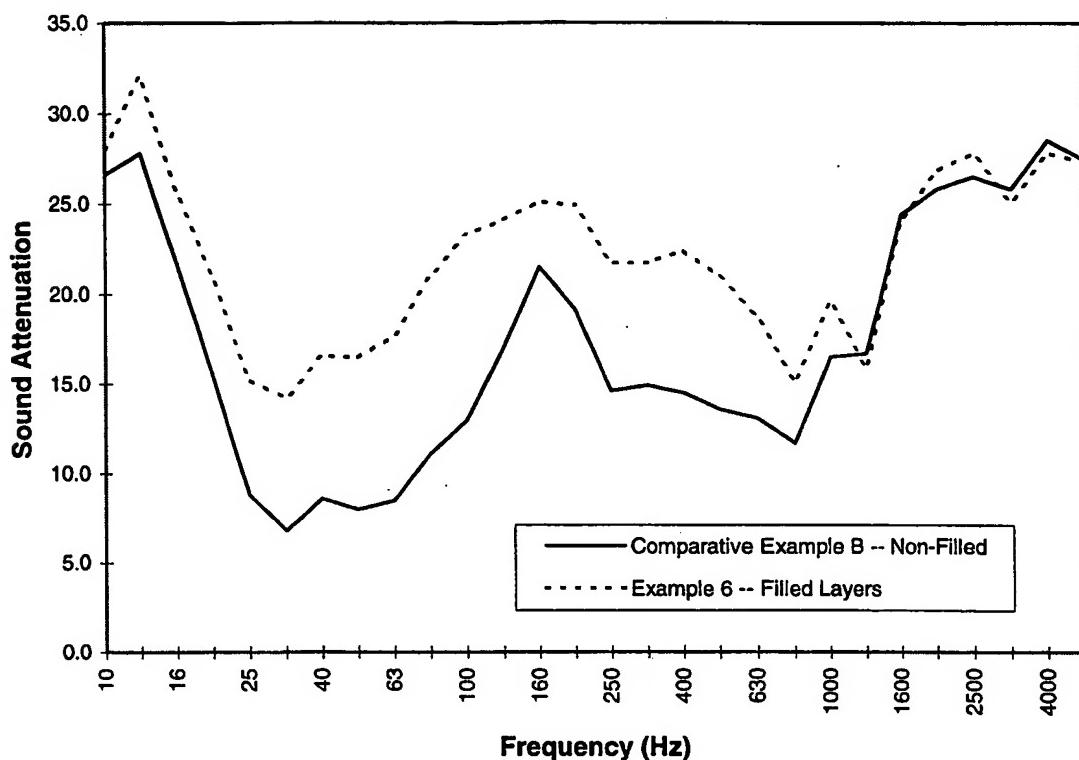
39. A porous polymeric material prepared by polymerizing the high internal phase emulsion of Claim 1 while in contact with a non-HIPE material such that the non-HIPE material becomes attached to the porous polymeric material during polymerization.

40. The polymeric material of Claim 39 wherein the non-HIPE material is a  
5 porous polymeric material, a non-woven material, or a polymeric film swellable with the external phase of the emulsion.

41. The polymeric material of Claim 40 wherein the porous polymeric material is a polyurethane foam, the non-woven material is a polypropylene non-woven tissue, and the polymeric film-swellable with the external phase of the emulsion is a  
10 polystyrene when using a water-in-oil emulsion with styrene in the oil phase.

42. A multilayer polymeric foam comprising at least two layers, each layer being either physically or structurally different from that of a contiguous layer and at least one layer being formed from a high internal phase emulsion having one or more insoluble filler, at least 70 volume percent of an internal phase and less than 30 volume percent of an  
15 external phase containing one or more vinyl polymerizable monomers and having a non-HIPE material between one or more layers and/or on one or both surface(s).

Figure 1



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16596

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C08F2/32 C08F2/ C08J9/28 B32B5/18

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X		1-9, 20-28, 30-32

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

<sup>a</sup> Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16596

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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